Errors in calculated molecular refractivities in orthorhombic crystals. By M. A. LASHEEN and S. TADROS, *Physics Department, Faculty of Science, Alexandria University, Alexandria, Egypt*

Expressions are obtained for the variances and relative uncertainties of the molecular refractivities in the case of orthorhombic crystals. It is deduced that when the ratios of the gram molecular refractivities are nearly equal to the corresponding ratios of the squares of the direction cosines of one of the molecular principal axes, the relative molecular refractivity uncertainties along the other two molecular principal axes will be relatively large.

The problem of the errors in the susceptibilities of orthorhombic crystals has previously been studied by us (Lasheen & Tadros, 1968), and it was noticed that, in certain cases, slight experimental errors in the measurement of crystal magnetic anisotropies would lead to relatively large uncertainties in the calculated relative molecular susceptibilities. In the present work the effect of the experimental errors in the case of the molecular optical refractivities of the same type of crystals is studied.

The experimental method usually applied for the determination of the molecular refractivities starts with measurement of the principal refractive indices (n_a, n_b, n_c), and hence the corresponding gram molecular refractivities (R_a, R_b, R_c) are deduced from the Lorentz–Lorenz equation, namely

$$R = \frac{(n^2-1)}{(n^2+2)} \cdot \frac{M}{D},\tag{1}$$

where n is the principal refractive index along a certain axis, R the gram molecular refractivity along the same axis, M the molecular weight and D the density. Ignoring the slight effect due to the uncertainties in the values of M and D, an experimental error δn would result in an uncertainty δR in the calculated value of R given by

$$\delta R = \frac{6n}{(n^2+2)^2} \cdot \frac{M}{D} \cdot \delta n.\tag{2}$$

The molecular refractivities (r_L, r_M, r_N), where r_L is along the length of the molecule, r_M along its breadth and r_N normal to its plane, may thus be deduced from the relation:

$$\begin{pmatrix} R_a \\ R_b \\ R_c \end{pmatrix} = \begin{pmatrix} \alpha_1^2 & \alpha_2^2 & \alpha_3^2 \\ \beta_1^2 & \beta_2^2 & \beta_3^2 \\ \gamma_1^2 & \gamma_2^2 & \gamma_3^2 \end{pmatrix} \begin{pmatrix} r_L \\ r_M \\ r_N \end{pmatrix}\tag{3}$$

where

$$\begin{aligned}
\alpha_1^2 &= \sum L_1^2; & \alpha_2^2 &= \sum L_2^2; & \alpha_3^2 &= \sum L_3^2 \\
\beta_1^2 &= \sum M_1^2; & \beta_2^2 &= \sum M_2^2; & \beta_3^2 &= \sum M_3^2 \\
\gamma_1^2 &= \sum N_1^2; & \gamma_2^2 &= \sum N_2^2; & \gamma_3^2 &= \sum N_3^2,
\end{aligned}$$

(L_1, M_1, N_1), (L_2, M_2, N_2) and (L_3, M_3, N_3) being the direction cosines of the molecular principal axes with respect to the crystal axes, the summation being taken over the independently oriented molecules in the unit cell.

Thus

$$r_L = \frac{D_1}{\Delta}; \quad r_M = \frac{D_2}{\Delta}; \quad r_N = \frac{D_3}{\Delta}\tag{4}$$

where Δ is the direction cosine determinant given by

$$\Delta = \begin{vmatrix} \alpha_1^2 & \alpha_2^2 & \alpha_3^2 \\ \beta_1^2 & \beta_2^2 & \beta_3^2 \\ \gamma_1^2 & \gamma_2^2 & \gamma_3^2 \end{vmatrix}$$

while the determinants D_1, D_2 and D_3 are respectively given by

$$D_1 = \begin{vmatrix} R_a & \alpha_2^2 & \alpha_3^2 \\ R_b & \beta_2^2 & \beta_3^2 \\ R_c & \gamma_2^2 & \gamma_3^2 \end{vmatrix}; \quad D_2 = \begin{vmatrix} \alpha_1^2 & R_a & \alpha_3^2 \\ \beta_1^2 & R_b & \beta_3^2 \\ \gamma_1^2 & R_c & \gamma_3^2 \end{vmatrix};$$

$$D_3 = \begin{vmatrix} \alpha_1^2 & \alpha_2^2 & R_a \\ \beta_1^2 & \beta_2^2 & R_b \\ \gamma_1^2 & \gamma_2^2 & R_c \end{vmatrix}.\tag{5}$$

Substituting from (5) into (4)

$$\left. \begin{aligned}
r_L &= \frac{1}{\Delta}(a_1 R_a + b_1 R_b + c_1 R_c) \\
r_M &= \frac{1}{\Delta}(a_2 R_a + b_2 R_b + c_2 R_c) \\
r_N &= \frac{1}{\Delta}(a_3 R_a + b_3 R_b + c_3 R_c)
\end{aligned} \right\}\tag{6}$$

where

$$\begin{aligned}
a_1 &= \beta_2^2\gamma_3^2 - \gamma_2^2\beta_3^2; & b_1 &= \gamma_2^2\alpha_3^2 - \alpha_2^2\gamma_3^2; & c_1 &= \alpha_2^2\beta_3^2 - \beta_2^2\alpha_3^2 \\
a_2 &= \beta_3^2\gamma_1^2 - \gamma_3^2\beta_1^2; & b_2 &= \gamma_3^2\alpha_1^2 - \alpha_3^2\gamma_1^2; & c_2 &= \alpha_3^2\beta_1^2 - \beta_3^2\alpha_1^2 \\
a_3 &= \beta_1^2\gamma_2^2 - \gamma_1^2\beta_2^2; & b_3 &= \gamma_1^2\alpha_2^2 - \alpha_1^2\gamma_2^2; & c_3 &= \alpha_1^2\beta_2^2 - \beta_1^2\alpha_2^2.
\end{aligned}$$

Thus the uncertainties in the values of the molecular refractivities r_L, r_M and r_N are given by

$$\left. \begin{aligned}
\delta(r_L) &= \frac{1}{\Delta}[|a_1|\delta(R_a) + |b_1|\delta(R_b) + |c_1|\delta(R_c)] \\
\delta(r_M) &= \frac{1}{\Delta}[|a_2|\delta(R_a) + |b_2|\delta(R_b) + |c_2|\delta(R_c)] \\
\delta(r_N) &= \frac{1}{\Delta}[|a_3|\delta(R_a) + |b_3|\delta(R_b) + |c_3|\delta(R_c)]
\end{aligned} \right\}\tag{7}$$

while the relative uncertainties $\delta(r_L)/r_L$, $\delta(r_M)/r_M$ and $\delta(r_N)/r_N$ are given by

$$\left. \begin{aligned}
\frac{\delta(r_L)}{r_L} &= \frac{1}{D_1}[|a_1|\delta(R_a) + |b_1|\delta(R_b) + |c_1|\delta(R_c)] \\
\frac{\delta(r_M)}{r_M} &= \frac{1}{D_2}[|a_2|\delta(R_a) + |b_2|\delta(R_b) + |c_2|\delta(R_c)] \\
\frac{\delta(r_N)}{r_N} &= \frac{1}{D_3}[|a_3|\delta(R_a) + |b_3|\delta(R_b) + |c_3|\delta(R_c)].
\end{aligned} \right\}\tag{8}$$

If it happens that the ratios of the crystal gram molecular refractivities are nearly equal to the corresponding ratios of the mean squares of the direction cosines of one of the molecular principal axes, two of the relative molecular refractivity uncertainties, those along the two other molecular principal axes, will be relatively large, *e.g.* if $R_a:R_b:R_c \simeq \alpha_1^2:\beta_1^2:\gamma_1^2$, then, as seen from equation (5), the determinants D_2 and D_3 will be very small, and conse-

quently, from equation (8), $\delta(r_M)/r_M$ and $\delta(r_N)/r_N$ will have rather high values.

Reference

LASHEEN, M. A. & TADROS, S. (1968). *Acta Cryst.* A24, 287–288.

A new analytic approximation to atomic incoherent X-ray scattering intensities.

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A new analytic approximation to atomic incoherent X-ray scattering intensities is proposed. Unlike other approximations in the literature, the present function has the correct asymptotic behaviour at both large and small values of *s*. Fits to the incoherent intensities calculated by Cromer are presented for all atoms from He through Am.

Several analytic approximations to the intensity of the incoherent scattering of X-rays by N-electron atoms are available in the literature (Furukawa, Orton, Hamor & Williams, 1963; Rodriguez & Pings, 1965; Hajdu, 1971, 1972; Palinkas, 1972).

The more accurate approximations are those of Hajdu (1971, 1972) and of Palinkas (1972). Hajdu's function is given by

$$I_{\text{inc}}(s) = [Z - I_{\text{coh}}(s)Z^{-1}] [1 - M \exp(-Ks) + M \exp(-Ls)] \quad (1)$$

where Z is the atomic number, $s = \lambda^{-1} \sin \theta$, θ is twice the scattering angle, $2\pi/\lambda$ is the propagation constant of the X-ray, and

$$I_{\text{coh}}(s) = [F(s)]^2 \quad (2)$$

is the intensity of the coherent scattering where the form factor, $F(s)$, is approximated by

$$F(s) = \sum_{i=1}^{4} A_i \exp(-B_i s^2) + C. \quad (3)$$

Palinkas (1972) uses the following approximation

$$I_{\text{inc}}(s) = Z[1 - a(1 + bs)^{-c}]. \quad (4)$$

Neither of the above functions has the correct asymptotic behavior either for large or for small values of s. The small-s behaviour of the total scattered intensity is known to be (Benesch & Smith, 1973)

$$I_{\text{tot}}(\mu) = N^2 - \mu^2 \langle r_{12}^2 \rangle/3 + O(\mu^4) \quad (5)$$

where $\mu = 4\pi s$, and the small-s behaviour of the form factor is known to be (Benesch & Smith, 1973)

$$F(\mu) = N - \mu^2 \langle r^2 \rangle/6 + O(\mu^4). \quad (6)$$

Hence the small-s behaviour of the incoherent scattering function is

$$I_{\text{inc}}(s) = a_2 s^2 + a_4 s^4 + \ldots \quad (7)$$

where $a_2 = 16\pi^2(N\langle r^2 \rangle - \langle r_{12}^2 \rangle)/3$. The large-$s$ behaviour of the incoherent scattering function has been shown (Smith, 1970) to be

$$I_{\text{inc}}(s) = N + b_4 s^{-4} + b_6 s^{-6} + \ldots \quad (8)$$

In this work we propose a new analytic approximation to the incoherent scattering function:

$$I_{\text{inc}}(s) = N[1 - (1 + as^2 + bs^4)(1 + cs^2 + ds^4)^{-2}]. \quad (9)$$

Of course, for neutral atoms $N = Z$. As can be easily verified, equation (9) has the correct asymptotic behaviour for both large and small values of s.

Non-linear least-squares fits, over the range $0 \le s \le 8.0$, of equation (9) to the $I_{\text{inc}}(s)$ values calculated by Cromer & Mann (1967) and Cromer (1969) have been carried out with the algorithm of Fletcher (1971). Table 1 lists values of the parameters $a, b, c,$ and d for all the atoms from He through Am. A measure of the 'goodness-of-fit', ε, is also listed in Table 1 for each atom. It is defined by

$$\varepsilon = 100[\sum_{i=1}^{k} \delta_i^2/(k-1)]^{1/2}/N \quad (10)$$

where δ_i are the deviations. ε can be considered to be a standard percent deviation because $N = \lim_{s \to \infty} I_{\text{inc}}(s)$. Table 1 shows that ε does not exceed $\sim 2\%$ for any of the atoms except Li. It should be noted that global optimization is currently impossible (Powell, 1970) and hence the parameters listed in Table 1 cannot be considered as defining anything better than a local minimum. Table 2 shows the typical quality of the fits for atoms of low ($Z=7$), medium ($Z=46$), and high ($Z=88$) atomic numbers.

A perusal of Table 1 shows that the fits worsen with increasing atomic number. For atoms of low and medium atomic number the overall quality of the fits obtained is comparable to the fits of Hajdu (1972) and Palinkas (1972). For atoms of high atomic number the fits are somewhat inferior to those of Palinkas (1972). However equation (9)